MIXED - LIGAND COMPLEXES OF CADMIUM WITH SOME AMINO ACIDS AND PYRIDOXINATE (VITAMIN B6).

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The reduction of mixed-ligand complexes formed by cadmium (II) with some amino acids (tryptophan, isoleucine, aspartic acid, lysine and valine) and pyridoxinate has been investigated polarographically. The stability constants are discussed from the point of view of steric, electrostatic and statistical considerations.

Due to the close association with life and related activities, pyridoxine has rightly attracted the attention of research workers in recent years for co-ordination studies, and its polarographic behaviour. Some of its derivatives have been investigated by Manousek and Zuman[1]. The mixed ligand complexes of cadmium (II) with amino acids and other ligands have been studied by many workers [2-4]. The survey of literature reveals that there is no reference which deals with the polarographic behaviour of mixed ligand complexes of Cd(II) with the above cited amino acids and pyridoxine. Hence the title investigation has been undertaken.

EXPERIMENTAL

All chemicals used were of AnalaR grade and all solutions were prepared in air free conductivity water. Potassium Nitrate was used as supporting electrolyte to maintain ionic strength constant at 1.0 M; 0.004% gelatin in the final solution sufficed as a maxima suppresor. Experiments were performed with 0.5 mM Cadmium. The pH of all the solutions was maintained at 9.2 ± 0.1 with an Elico digital pH meter (Model LI-120). Purified nitrogen was passed through the solution to remove the oxygen. Polarograms of the solutions were taken using a manual polarograph. Saturated calomel electrode was used as reference electrode. The capillary had the following characteristics; m = 1.96 mg/sec , t = 4.05 sec/drop and h_{corr} = 40.0 cm. (at 303 ± 1° K in 0.1M KNO_3 in open circuit).

RESULTS

The Simple Systems

The stepwise formation constants of the complexes of Cd(II) pyridoxinate, tryptophanate, isoleucinate, aspartate, lysinate and valinate were determined seperately under identical conditions before the study of mixed ligand systems. The results are summarized in Table 1.

TABLE 1

STABILITY CONSTANTS OF SIMPLE COMPLEXES OF Cd(II) WITH AMINO ACIDS AND PYRIDOXINATE

$[Cd^{++}]$ = 0.5 m Molar pH 9.2 μ = 1.0M with KNO_3
m = 1.96 mg/sec t = 4.05 sec/drop at h = 40 cms.

T = 303 ± 1°K

System	log β_1	log β_2	log β_3
Cd(II)-Pyridoxinate	1.40	2.34	
Cd(II)-Tryptophanate	4.45	8.05	10.50
Cd(II)-Isoleucinate	4.00	7.00	9.00
Cd(II)-Aspartate	4.25	7.95	10.20
Cd(II)-Lysinate	3.70	6.90	8.95
Cd(II)-Valinate	3.65	6.60	8.40

The Mixed - Ligand Systems

The cadmium-tryptophanate-pyridoxinate, cadmium-isoleucinate-pyridoxinate, cadmium-aspartate-pyridoxinate, cadmium-lysinate -pyridoxinate and cadmium-valinate - pyridoxinate systems were studied by keeping the concentration of the weaker ligand (pyridoxinate) constant at 0.04 M or 0.2 M while varying the concentration of second ligand.

Solution containing 5×10^{-4}M Cd^{2+}, 0.04 M [Pyr] and requisite amount of KNO_3, were polarographed at varying concentration of amino acid for each of the systems. The free ligand concentration for each system has been calculated with the help of pH of the solution, pK value and amount of the ligand. The pK values of amino acids were calculated by the method of Albert and Serjeant[6] at 303 ± 1K. In all cases, the single well defined and diffusion controlled wave had a slope of 30 ± 2 mV for the log plots indicating that the reduction is reversible and involves two electrons. The experiment was repeated with a pyridoxinate concentration of 0.2 M.

As the concentration of tryptophanate, isoleucinate, aspartate, lysinate and valinate is increased,

TABLE 2

CADMIUM TRYPTOPHANE-PYRIDOXINATE SYSTEM

$[Cd^{++}]$, 0.5 mM $-E_{1/2}$ = 0.580V vs SCE

[X] x10⁴M	$\Delta E_{1/2}$ V	$\log \frac{I_M}{I_C}$	F_{00} x10⁻²	F_{10} x10⁻⁴	F_{20} x10⁻⁸	F_{30} x10⁻¹⁰
[Pyr] = 0.04 M						
5.23	0.0555	0.0183	0.73	13.51	1.46	3.06
7.86	0.0640	0.0310	1.45	18.15	1.56	3.31
13.09	0.0765	0.0310	3.77	28.62	1.74	3.36
23.57	0.0925	0.0350	12.96	54.89	2.08	3.31
39.28	0.1080	0.0350	42.48	108.09	2.60	3.31
78.57	0.1310	0.0362	248.07	315.70	3.94	3.36
104.76	0.1410	0.0375	535.27	510.92	4.82	3.36
130.95	0.1490	0.0375	987.94	754.42	5.72	3.38
157.13	0.1555	0.0400	1634.88	1040.45	6.58	3.36
183.32	0.1610	0.0428	2507.67	1367.91	7.43	3.34
A = 2.35 (cal) B = 5.90×10^4 , C = 1.3×10^8 , D = $(3.34 + 0.04) \times 10^{10}$						
[Pyr] = 0.2 M						
5.23	0.0685	0.0230	2.00	3.54	2.18	3.44
7.86	0.0750	0.0398	3.43	4.18	2.26	3.31
13.09	0.0850	0.0465	7.49	5.61	2.45	3.44
23.57	0.0985	0.0535	21.41	9.02	2.81	3.44
39.28	0.1120	0.0590	60.99	15.49	3.33	3.39
78.57	0.1330	0.0625	307.19	39.08	4.67	3.40
104.76	0.1425	0.0625	636.03	60.70	5.57	3.41
130.95	0.1500	0.0652	1136.84	86.80	6.45	3.40
157.13	0.1565	0.0652	1870.49	119.03	7.42	3.45
183.32	0.1615	0.0765	2815.82	153.59	8.25	3.41
A = 14.80 (cal), B = 2.4×10^5 , C = 2×10^8 , D = $(3.41 \pm 0.1) \times 10^{10}$						

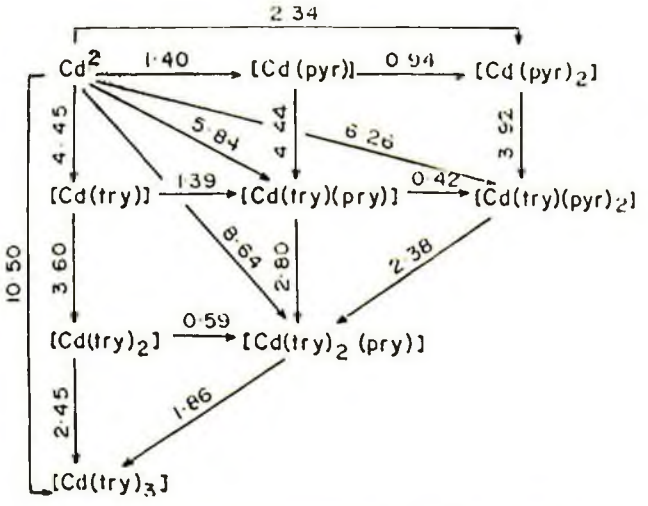
the half wave potential shifts towards more negative values. This shift in half-wave potential is greaterin the presence of pyridoxinate than in its absence. It indicates mixed-ligand complex formation. The Schaap and McMasters[7] treatment was applied for calculating the F functions and Leden's[8] graphical extrapolation method to calculate the A, B, C and D at two different [Pyr] values. The F_{ij} function for a typical system are given (Table 2). The stability constants were evaluated from the values of A, B, C and D. The stability constants log β_{11} , log β_{12} and β_{21} of all the systems are presented in Table 3. The stability constant equilibria are presented in the Schemes (I-V).

DISCUSSION

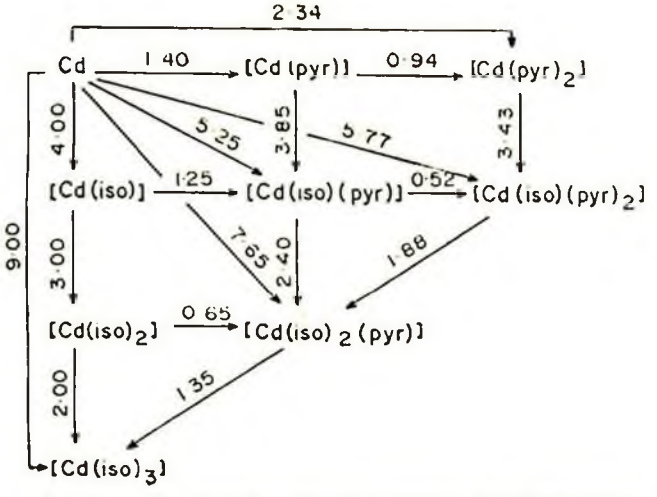
The stability of ternary complexes can be explained with the help of Schemes (I-V). The tendency of [Cd(pyr)] and [Cd(a.a.)] to add a second ligand can be compared. The log K values are (0.94,1.39), (0.94,1.25), (0.94, 1.45), (0.94, 1.49) and (0.94, 1.35) for tryptrphanate-pyridoxinate, isoleucinate pyridoxinate, aspartate-pyridoxinate, lysinate-pyridoxinate and valinate-pyridoxinate systems respectively and show that the mixed-ligand complexation is favoured. The log K values for addition of amino acid to [Cd(Pyr)] and [Cd(a.a.)] are (4.44,3.60), (3.85,3.00), (4.30,3.70), (3.79,3.20) and (3.60,2.95) for all the systems respectively. This shows that the mixed complex formation is affected by statistical factors.

The log K values for addition of amino acids to [Cd(Pyr)], [Cd(a.a.)(Pyr)] and [Cd(a.a.)] are (3.92, 2.80 and 2.45), (3.43, 2.40 and 2.00), (3.77, 2.70 and 2.25), (3.36, 2.40 and 2.05) and (3.19, 2.20 and 1.80) for all the systems respectively and show that the addition of amino acids is preferred to a weaker ligand (pyridoxinate).

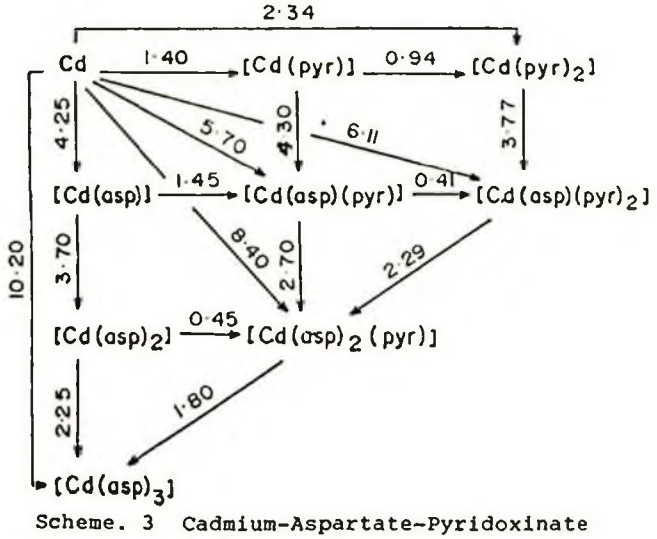
The stabilities of simple and mixed complexes can be compared by measuring the disproportionation constant K_d for the equilibria.



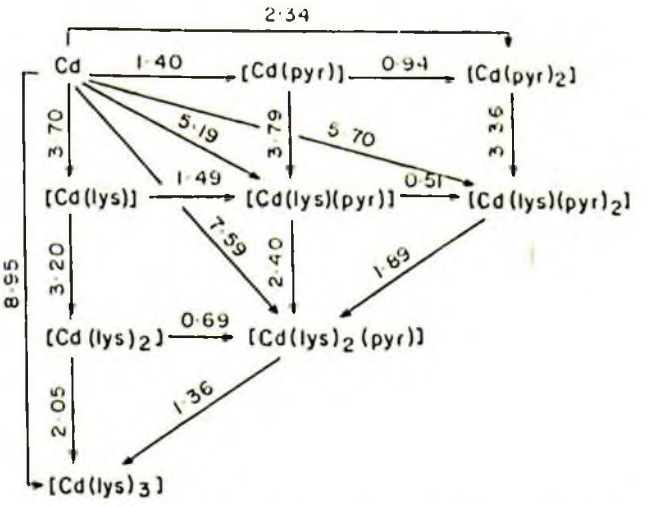
Scheme. 1 Cadmium-Tryptophanate-Pyridoxinate System.



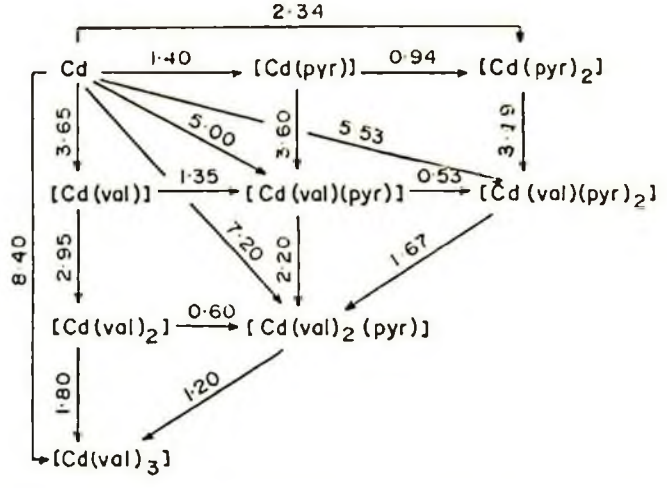
Scheme. 2 Cadmium-Isoleucinate-Pyridoxinate System.



Scheme. 3 Cadmium-Aspartate-Pyridoxinate System.



Scheme. 4 Cadmium-Lysinate-Pyridoxinate System



Scheme. 5 Cadmium-Valinate-Pyridoxinate System

TABLE 3

STABILITY CONSTANTS OF MIXED - LIGAND COMPLEXES OF Cd(II) WITH AMINO ACIDS AND PYRIDOXINATE

System	log β_{11}	log β_{12}	log β_{21}
Cd-try-pyr	5.84	6.26	8.64
Cd-isoleu-pyr	5.25	5.77	7.65
Cd-asp-pyr	5.70	6.11	8.40
Cd-lys-pyr	5.19	5.70	7.59
Cd-val-pyr	5.00	5.53	7.20

However the observed values are found to be $10^{-1.29}$, $10^{-1.11}$, $10^{-1.12}$, $10^{1.14}$ and $10^{-1.06}$ for all the systems respectively. These values are smaller than 0.25, which account for the stability of the mixed ligand complexes.

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